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# BIOMATERIALS SCIENCE

## An Introduction to Materials in Medicine

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TABLE I Typical Mechanical Properties of Polymer-Ceramic Composites [Three-Point Bending]

Regime	Ultimate strength (MPa)	Modulus (GPa)
DMAA	772	55
Dynamolite	938	76
Epoxy	535	20
Siloxane	207	24
Tyred	—	14
Tubophane	239	14

### SUMMARY

Biomedical composites have demanding properties that allow few, if any, off-the-shelf materials to be used. The designer must start over from scratch. Consequently, few biomedical composites are yet in general clinical use. Those that have been developed to date have been tailored for fairly primitive materials with simple designs. They are simple, inexpensive or cheap-to-fabricate, or perhaps-aesthetically systems with no attempts made to react or bond the phases together. Such bonds may be accomplished by abetting the surface texture of the fibers or by interlocking coupling agents (i.e., monomers). Many resins will do this and more. However, fiber-polymer composites developed with a bidirectional bonded layer composed of carbon-polymer composite covering the core. These regions were created in an effort to bring price polypropylene (Fig. 8).

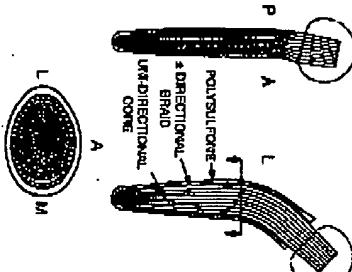


FIG. 8 Construction details of a fibrous core of a composite resin. Reproduced with permission from F. P. Ayala, A. M. Williams, J. A. Lanza, J. A. Marquez, and J. A. Vaca, *Oral Chelotherapy*, 1991, 147-202, 28 (A. M. Williams, Ed.), Chapman and Hall.

Properties provide an opportunity for a natural bone remodeling response to enhance implant stability.

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Because of the high development costs and the small market available, to date, few materials have been designed specifically for biomedical use. Biomedical composites, because of their unique requirements, will probably be the first general class of materials developed exclusively for implantation purposes.

Agrawal, B. D., and Ahrendsen, J. G. (1970). *Analytical and Performance of Fiber Composites*. Wiley-Syntex, New York.

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### 1.9 THERMISATION, COATINGS, AND COATINGS

On the other hand, are controlled largely by the surface chemistry and structure (see Chapters 1.3 and 3.7). The rationale for short surface modification of biomaterials is therefore straight-forward: to retain the key physical properties of a biomaterial while modifying only the outermost surface to influence the biological interaction. If such surface modifications are properly efficient, the mechanical properties and functionality of the device will be unaffected, but the surface-tissue-related biocompatibility will be improved or changed.

Materials can be surface-modified by using biological or physicochemical methods. Many biodegradable surface modifications are covered in Chapter 2.1. Generalized examples of physicochemical surface modifications, the focus of this chapter, are illustrated schematically in Fig. 1. Surface modification with a nanoparticle-thick film has numerous applications for surface-modified biomaterials and it is described in detail in Chapter 2.1.1. Generalized examples of the mechanical properties and functionalities of the device will be improved or changed.

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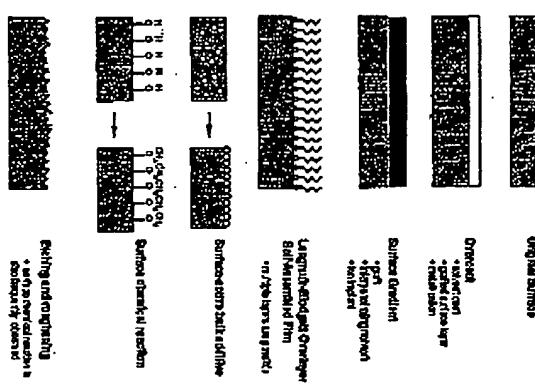
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### 2.9 TORN FLAPS, GRAFTS, AND COATINGS

Bandy, D., Ramam, and Allen & Hoffman

Many efforts go into the design, synthesis, and fabrication of biomaterials and devices to ensure that they have the optimum mechanical properties, durability, and biocompatibility. To take a few examples, a hip joint should withstand high stress, a bone-implant should have the requisite biocompatibility, and the bonding of a bone graft to an artificial heart should fix the materials given its weight.

The biological response to biomaterials and devices, on



Original Surface → Direct surface treatment → Surface coating → Surface coating with nanoparticle-thick film

TABLE 1 Examples of Surface-Modified Biomaterials

To Modify Blood Compatibility	Polymer	Steel	Ceramic	None
Orthodox group attachment to surface (fibrinogen affinity)				
Silane-modifying block copolymer additive				
Tissue fluoropolymer deposition				
Radiation grafted hydrogels				
Chemically modified oligopeptide to heparin-like activity				
To Improve Cell Adhesion and Growth				
Oxidized polyurethane surface				
Aromatic plasma-treated surface				
Fluorocopolymer deposition (reduce oxidative reduction to NO <sub>x</sub> )				
To Control Protein Adsorption				
Surface with immobilized polyethylene glycol (reduce adsorption)				
Toward PA-100, dabs, mabs (reduce adsorption and repulsion)				
Aldehydic chromogenic pentolites (reduce desorption or thin surface cross-linked enzyme k <sub>d</sub> ) (reduce adsorption)				
To Improve Lubricity				
Surfactant-coated surfaces				
Surfactant-coated hydrogels				
Surfactant-modified polymeric networks				
To Improve Wear Resistance and Corrosion Resistance				
Ion implantation				
Diamond deposition				
Abstraction				
To Alter Transport Properties				
Diam deposition (semicon, fluoropolymer, aluminum)				
To Modify Material Characteristics				
Flame pyrolysis (imidization, heat)				
Solvent extraction (solvent or condensate)				

Surface modifications fall into two categories: (1) chemically or physically altering the atom, compound, or molecule in the existing surface (removal, addition, chemical modification), or (2) interacting the existing surface with a material having a different composition (coating, grafting, thin film deposition). A few general principles provide guidance when undertaking surface modification.

### This Surface Modification

These surface modifications are desirable. The modified zone on the surface of the material should be as thin as possible. Modified surface layers that are too thick can change the me-

chanical and functional properties of the material. Thick coatings are often more subject to delamination. How thin should a surface modification be? Ideally, alteration of only the outermost nanolayer (3–10 Å) should be sufficient. In practice, there often are thin, thin film will be necessary since it is difficult to ensure that all of the original surface is uniformly covered when coatings and treatments are done. Also, extremely thin layers may be more subject to surface erosion (degradation) and mechanical erosion. Since coatings potentially have a specific thickness, for example, thin filaments of LB film is related to the length of the surfactant molecules that complete them (25–50 Å). Other coatings, such as polymer-based proteins-repellent layers, may require a minimum thickness (i.e., a dimension related to the molecular weight of deamino) to function. In general, surface modifications should be the minimum thickness needed for uniformity, durability, and functionality, but no thicker. This must be experimentally defined for each system.

### Deformation/Fast Resistance

The surface-modified layer should be robust to deformation. This is achieved by covalently bonding the modified region to the substrate, increasing the cross-section of the resistance and the surface film in an interfacial zone, lowering a "capillary bridge," ("pinch") effect at the interface, or increasing appropriate functional groups for strong intermolecular adhesion between a substrate and an overlayer (Wu, 1987).

### Surface Rearrangement

Surface rearrangement occurs readily. Surface chemistry and structures can change as a result of the diffusion or translation of surface atoms or molecules in response to the external environment (see Chapter 1.3 and Fig. 2 in this chapter). A newly formed surface chemistry can originate from the surface ions the bulk, or molecules from the bulk can diffuse to cover the surface. Such rearrangements occur in metallic and other biological systems, as well as in polymer systems. Terms such as "recrystallization," "relaxation," and "surface segregation" are often used to describe mobility-related alterations in surface structure and chemistry (Ritter and Yoon, 1988; Gurbaxi et al., 1987; Sonnerup, 1990, 1991). The driving force for these surface changes is thermodynamic— to minimize the free enthalpy energy. However, individual atoms or molecular mobility must exist for this surface changes to occur in reasonable periods of time. For a modified surface to remain as it was designed, surface renewal must be prevented or inhibited. This can be done by cross-linking, sterically blocking the ability of surface structures to move, or by incorporating a rigid, impermeable layer between the substrate material and the surface modification.

### GENERAL PRINCIPLES

2.9 THIN FILMS, CRAFTS, AND COATINGS				
TABLE 2 Physical and Chemical Surface Modification Methods				
	Polymer	Steel	Ceramic	None
Resonance casting				
Sputter coating				
Laser/UV-Bigert Poly deposition				
Surface-active additives				
Vapor deposition of carbon and metals				
Vapor deposition of borazine (Pyrolytic)				
Covalently attached coatings				
Radiation grafting (electron accelerator and gamma)				
Fluorinating (UV and visible radiation)				
Film (gas discharge (O <sub>3</sub> , microwave, arc, etc.)				
Gas phase deposition				
Ion beam sputtering				
Chemical vapor deposition (CVD)				
Chemical grafting (O <sub>3</sub> , ozonation + grafting)				
Biological modification (biomimetic immobilization)				
Modifications of the original surface				
In item existing film, layer, surface, ceramic				
In item deposited film, layer, ceramic				
Electro coating (e.g., anodizing,阳极化,阳极氧化, water				
Coatings discharge (in air)				
In cathodic				
UV irradiation				
Chemical reaction				
Nonspecific condition (e.g., ozone)				
Electron beam oxidation (condensation, reduction)				
Current area etching (disengaging, annihilation)				
Gas polymer with local damage				

General methods to modify the surface of materials are illustrated in Fig. 1, with many examples listed in Table 2. A

modification schematic. The potential for surface scission to occur during surface modification is very high. The reaction should be monitored to ensure that the intended surface is indeed being formed. Since conventional physical methods are often not sensitive enough to detect surface modification, specific surface analytical tools are called for (Klimper, 1981).

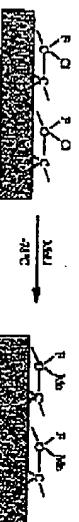
### Commercializability

The end products of biomaterials research are devices and materials that are man made and not in humans. A surface modification that is too complex will be difficult and expensive to commercialize. It is best to minimize the number of steps in a surface modification process and to design each step to be relatively inexpensive to small changes in reaction conditions.

### METHODS FOR MODIFYING THE SURFACES OF MATERIALS

There are hundreds of chemical reactions that can be used to modify the chemistry of a surface. In the context of this chapter, chemical reactions are those reactions performed with reagents that react with atoms or molecules on a new type. Chemical reactions can be classified as non-specific and specific. Non-specific reactions have a distribution of different functional groups on the surface. An example of a non-specific surface chemical modification is the atomic and radical oxidation of polymeric surfaces. Other examples include the conversion of poly(methyl methacrylate) (PMMA) to poly(acrylic acid) (PAA) via UV-COOH (RCOOH) treatment of material in aqueous, aqueous

**A. Alkylation of poly(methacrylate(methylmethacrylate))**



**B**

**Triboroacetic anhydride reaction of a hydroxyplated surface**



**C**

**Glycidyl Group Introduction into a poly(oxazone)**

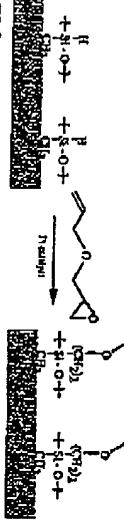


FIG. 2. Some specific chemical reactions to modify surfaces. (A) Dau and Lach, in: *Macromolecules* 19, 1976; (B) Chilkoti et al., *Chem. Mater.* 3, 11, 1391; (C) Cooper et al., *Adv. Polym. Sci.* 74, 177, 1982.

nitrogen, carbon dioxide, or water vapor environment; and the extraction of metal surfaces to a mixture of stanobene.

Specific chemical surface reactions change only one functional group into another with a high yield and few side effects. Examples of specific chemical surface modifications for polymers are presented in Fig. 2.

#### Radiation Grafting and Photografting

Radiation grafting and related methods have been widely used for the surface modification of biomaterials, and complete literature reviews are available (Kramer, 1970; Hoffman et al., 1984; Sano, 1990). Within this category, three types of structures can be distinguished: (1) surface-initiated polymerization methods on a rubber latex, (2) surface-initiated polymerization methods on a solid support, and (3) surface-initiated polymerization methods in a solution (monomer + solvent).

Monomer (2) is often exposed to a radiation source. (2) The substrate material can also be exposed to the radiation under air at room temperature or at low temperatures. In this case, the monomer can react with an amine to form amines, which can then react with carboxylic acids to form esters. (3) Finally, the reaction can take place in air or nitrogen, leading to the formation of peroxide groups on the surface. Heating the material to be grafted in the presence of a monomer or the addition of a reducing agent ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) will decompose the peroxide groups to form free radicals that can initiate the graft polymerization.

Graft layers formed by competitive reaction of the substrate are often thick ( $> 1 \mu\text{m}$ ). However, they are well bonded to the substrate material. Since many polyfunctional monomers are available, a wide range of surface distributions can be obtained. Monomers or monomers can form unique graft copolymers (Ritter and Hoffman, 1980). For example, the hydrophilic

environment. The monomer reacts with the free radicals at the surface and propagates an after-reaction chain reaction, independent other monomers onto surface-grafted polymer.

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#### RGDO Plasma Deposited and Other Plasmas

##### Gas Processes

RGDO plasmas, as used for surface modifications, are low-pressure (isolated) gas environments typically at ambient (or slightly above ambient) temperature. They are also referred to as glow discharge or gas discharge depositions or treatments. Plasmas can be used to modify existing surfaces by plasma or existing treatments or, in a deposition mode, to overcoat surfaces and propagate an after-reaction chain reaction, independent other monomers onto surface-grafted polymer.

These direct reaction methods can be categorized: (1) in the monomer (radical) method, the substrate material is immersed in a solution (monomer + solvent); (2) the monomer (radical) that is then exposed to the radiation source; (3) the substrate material can also be exposed to the radiation under air at room temperature or at low temperatures. In this case, the monomer can react with an amine to form amines, which can then react with carboxylic acids to form esters. (4) Finally, the reaction can take place in air or nitrogen, leading to the formation of peroxide groups on the surface. Heating the material to be grafted in the presence of a monomer or the addition of a reducing agent ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) will decompose the peroxide groups to form free radicals that can initiate the graft polymerization.

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hydrophilic ratio of surfaces can be controlled by varying the ratio of a hydrophilic and a hydrophobic monomer in the grafting mixture (Ritter and Hoffman, 1980; Ritter et al., 1979).

Photoinitiated grafting (usually with visible or UV light) represents a unique subcategory of surface modifications for which there is growing interest. There are many approaches to effect this photoinitiated covalent coupling. For example, a phenyl ester group can be converted to a highly reactive nitroso upon UV exposure. This nitroso will quickly react with amino organic groups. If a hydrophilic polymer is prepared with phenyl ester side groups and the polymer is exposed simultaneously to UV light and a reactive polymer, an polymeric radical species, an hydroperoxymino-phenyl substituted polymer will be immobilized to the substrate (Kurata and Tomi, 1990).

Another method involves the coupling of a bisphenol-type molecule to a hydrophilic polymer (Danckwirt et al., 1991). In the presence of UV irradiation, the bisphenol is oxidized to a radical, which then can readily couple to many polymers.

Radiation, electron-, and photoinitiated have been increasingly used to bond hydrogels to the surfaces of hydrophilic polymers (Kaneko and Itoh, 1991; Danckwirt et al., 1991) [see also Chapter 5]. The protein interactions (Kaneko and Hoffman, 1975), cell adhesion (Ramer et al., 1975; Manuki and Hoffman, 1980), blood compatibility (Chaplin, 1983; Hoffman et al., 1983), and tissue reactions (Kerecsek, 1977) of hydrogel graft surfaces have been investigated.

#### 2.9. THERMAL GRaFTS AND COATINGS

##### TABLE 3 Biomedical Applications of Glow Discharge Plasma-induced Surface Modification Techniques

	1. Flame treatment (ashing)	2. Seeding	3. Crosslink surface modulus	4. Plasma treatment (etching) and plasma deposition	5. Burn layer film	6. Protective coating
Bioceramic	Bioceramic ablation of material from the environment	Health risks of bioceramics	Control drug delivery site			
Implant	Modify cell and protein surfaces	Improve biocompatibility	Protective surface layer on substrate			
Biomaterial			Bioceramic cell adhesion			
Bioplastic			Improve cell growth			
Prosthetic			Protective coating			

magnetic resonance (NMR) [Rajpiani and Dill, 1981], electron spectroscopy for chemical analysis (ESCA) [Goldschmid et al., 1979a,b], chemical derivatization media [Gorbachuk and Luttmann, 1978; Grotter and Chaudhury, 1990], chlorine et al., 1979a], and atomic absorption [Kasai, 1992].

11. Plasma-treated surfaces are useful when recovered from the reactor, offering an additional advantage for cost-effective production of medical devices.

It would be inappropriate to cite all these advantages without also discussing some of the disadvantages of plasma deposition on surface. First, the chemistry produced on surface can be ill-defined. For example, if inert fluorocarbon gas is introduced into the reactor, polytetrafluoroethylene will not be deposited on the surface. Rather, a complex, branched fluorocarbon polymer will be produced. This embossing of monomer structure has been addressed in studies dealing with retention of fluorocarbon structure in the final film [Lopez and Ritter, 1971, 1972]. Second, the apparatus used to produce plasma deposition polymers is expensive. A small laboratory-scale reactor will cost \$10,000-\$30,000, and a production reactor can cost \$100,000 or more. Third, a uniform distribution of particles can be a problem, and care must be exercised in preventing extraneous gases and plume off from entering the reaction zone. However, the advantages of plasma reaction outweigh these potential disadvantages by many orders of magnitude for current, or accomplishable by any method.

### THE NATURE OF THE PLASMA ENVIRONMENT

Plasma is electrically and molecularly dissociated gaseous environment. A plasma environment contains positive ions, and negative ions, free radicals, electrons, atomic emitters, and photons. Typical conditions within the plasma include an electron density of  $10^{11}$  to  $10^{12}$  cm $^{-3}$ , a temperature of 25–40°C, an ion energy of  $10^{-10}$  to  $10^{-12}$  eV, and an operating pressure of  $10^{-2}$  to  $10^{-3}$  torr.

A number of processes can occur on the substrate surface that lead to surface modification or deposition. These, a complex place between deposition and etching of the high-energy plasma species (Miyata, 1979). When deposition is more rapid than disappearance, the deposition will be observed. Because of its complex nature, the deposition process can result in substantial chemical and morphological changes to the substrate.

A number of mechanisms have been postulated for the deposition process. A selective gaseous environment may create free radicals and other reactive species on the substrate surface that react with and polymerize molecules from the gas phase. Alternatively, reactive small molecules in the gas phase may combine to form higher molecular weight units or particulates that may settle or precipitate onto the surface. Most likely the deposition observed is formed by some combination of these two processes.

### PRODUCTION OF PLASMA ENVIRONMENTS FOR DEPOSITION

#### FOR SURFACES

Many experimental variables relating both to reaction conditions and to the substrate characteristics that deposit are placed effect the final outcome of the plasma deposition process [Fig. 3]. A diagram of a typical industrially coupled radio frequency plasma reactor is presented in Fig. 3. The most significant that comprise this apparatus are a gas introduction system (control of gas mixing, flow rate, and flow of gas entering the reactor), a vacuum system (vacuum, and control of reaction pressure and inhibition of backstreaming of components from the pump), an argon gas system to efficiently couple energy into the gas phase within the reactor, and a reactor unit in which the samples are treated. Radio frequency, microwave, or microwave energy can be coupled to the gas phase. Devices for monitoring the molecular weight of the gas phase species (mass spectrometer), the optical emission from the plasma (plasma spectrometer), and the deposited film thickness (calorimeter, vibrating quartz crystal or balanced armato-com-

pendulum) are also used to directly monitor organic functional groups (e.g., amine, hydroxyl) on a surface that can be activated to attack biomaterials [see Chapter 2.1]. Certain organic environments can also be used to directly immobilize organic molecules such as enzymes. For example, a poly(ethylene glycol) block copolymer, uniformly distributed to polyethylene via the propylene glycol block, will adsorb to polyethylene via the propylene glycol block. If exposed to a oxygen plasma, the poly(ethylene glycol) block will be cross-linked, thereby leading to desorption and attachment of surface poly(ethylene glycol) chains [Goto et al., 1992].

### HIGH-TEMPERATURE AND HIGH-ENERGY PLASMA TREATMENTS

The plasma environment described here are of relatively low energy and low temperature. Consequently, they can be used to deposit organic layers on polymeric or inorganic substrates. Under higher energy conditions, plasma can effect unique and important inorganic surface modifications on homogeneous substrates. For example, flame spray deposition involves injecting a high-energy, relatively finely divided (~10 mesh) metal powder into a high-velocity plasma or flame. The method is usually employed to deposit particles onto a substrate and solidify rapidly (see Chapter 2.2 for additional information).

#### Slantabiosis

The proposed technology of a spin-lime surface modification reaction is illustrated in Fig. 4. Silane reactions can be

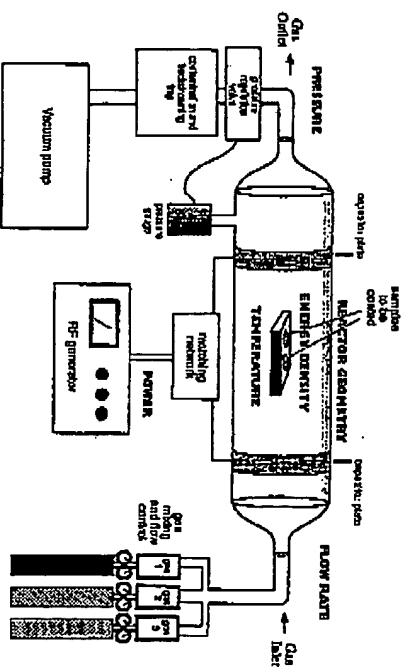


FIG. 3. A diagram of a typical industrially coupled RF plasma reactor. Apparatus requiring variables are indicated in bold capital letters.

TABLE 4. Silanes for Surface Modification of Biomaterials

X = Basal group	X
-Cl	- $(\text{CH}_2)_n\text{Cl}$
-OC $\text{OCH}_3$	- $(\text{CH}_2)_n\text{COOCH}_3$
- $(\text{CH}_2)_n\text{O}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{O}-$	- $(\text{CH}_2)_n\text{COO}-\text{C}(=\text{O})-\text{O}-$
- $\text{CH}_2\text{CH}_2$	- $\text{CH}_2\text{CH}_2$

#### Spin-Lime Deposition

The ion beam method [ions accelerated with energies ranging from  $10^3$  to  $10^5$  eV =  $10 \times 10^{-19}$  farads] can change the surface zone of a material to alter its surface properties. It is typically, but not exclusively, used with metals and other inorganic systems. Ions formed from most of the atoms in periodic table can be impinged, but not all provide useful modifications of the surface properties. Impinging potentials



**FIG. 4.** The chemistry of a physical film with an interface reaction. (A) Unmodified surface in contact with a silanol. (B) After interface reaction. (C) Surface resulting from attachment of a polymer chain. (D) After grafting a silane-modified polymer onto the surface. The "W" group in the other molecules stands for a polymer chain. (Reprinted with permission from the *Journal of Biomedical Materials Research*, Vol. 21, 1987, 101, 113, 121, 129, 137, 145, 153, 161, 169, 177, 185, 193, 197, 205, 213, 221, 229, 237, 245, 253, 261, 269, 277, 285, 293, 297, 301, 309, 317, 325, 333, 341, 349, 357, 365, 373, 381, 389, 397, 405, 413, 421, 429, 437, 445, 453, 461, 469, 477, 485, 493, 501, 509, 517, 525, 533, 541, 549, 557, 565, 573, 581, 589, 597, 605, 613, 621, 629, 637, 645, 653, 661, 669, 677, 685, 693, 697, 701, 705, 709, 713, 717, 721, 725, 729, 733, 737, 741, 745, 749, 753, 757, 761, 765, 769, 773, 777, 781, 785, 789, 793, 797, 801, 805, 809, 813, 817, 821, 825, 829, 833, 837, 841, 845, 849, 853, 857, 861, 865, 869, 873, 877, 881, 885, 889, 893, 897, 901, 905, 909, 913, 917, 921, 925, 929, 933, 937, 941, 945, 949, 953, 957, 961, 965, 969, 973, 977, 981, 985, 989, 993, 997, 1001, 1005, 1009, 1013, 1017, 1021, 1025, 1029, 1033, 1037, 1041, 1045, 1049, 1053, 1057, 1061, 1065, 1069, 1073, 1077, 1081, 1085, 1089, 1093, 1097, 1101, 1105, 1109, 1113, 1117, 1121, 1125, 1129, 1133, 1137, 1141, 1145, 1149, 1153, 1157, 1161, 1165, 1169, 1173, 1177, 1181, 1185, 1189, 1193, 1197, 1201, 1205, 1209, 1213, 1217, 1221, 1225, 1229, 1233, 1237, 1241, 1245, 1249, 1253, 1257, 1261, 1265, 1269, 1273, 1277, 1281, 1285, 1289, 1293, 1297, 1301, 1305, 1309, 1313, 1317, 1321, 1325, 1329, 1333, 1337, 1341, 1345, 1349, 1353, 1357, 1361, 1365, 1369, 1373, 1377, 1381, 1385, 1389, 1393, 1397, 1401, 1405, 1409, 1413, 1417, 1421, 1425, 1429, 1433, 1437, 1441, 1445, 1449, 1453, 1457, 1461, 1465, 1469, 1473, 1477, 1481, 1485, 1489, 1493, 1497, 1501, 1505, 1509, 1513, 1517, 1521, 1525, 1529, 1533, 1537, 1541, 1545, 1549, 1553, 1557, 1561, 1565, 1569, 1573, 1577, 1581, 1585, 1589, 1593, 1597, 1601, 1605, 1609, 1613, 1617, 1621, 1625, 1629, 1633, 1637, 1641, 1645, 1649, 1653, 1657, 1661, 1665, 1669, 1673, 1677, 1681, 1685, 1689, 1693, 1697, 1701, 1705, 1709, 1713, 1717, 1721, 1725, 1729, 1733, 1737, 1741, 1745, 1749, 1753, 1757, 1761, 1765, 1769, 1773, 1777, 1781, 1785, 1789, 1793, 1797, 1801, 1805, 1809, 1813, 1817, 1821, 1825, 1829, 1833, 1837, 1841, 1845, 1849, 1853, 1857, 1861, 1865, 1869, 1873, 1877, 1881, 1885, 1889, 1893, 1897, 1901, 1905, 1909, 1913, 1917, 1921, 1925, 1929, 1933, 1937, 1941, 1945, 1949, 1953, 1957, 1961, 1965, 1969, 1973, 1977, 1981, 1985, 1989, 1993, 1997, 2001, 2005, 2009, 2013, 2017, 2021, 2025, 2029, 2033, 2037, 2041, 2045, 2049, 2053, 2057, 2061, 2065, 2069, 2073, 2077, 2081, 2085, 2089, 2093, 2097, 2101, 2105, 2109, 2113, 2117, 2121, 2125, 2129, 2133, 2137, 2141, 2145, 2149, 2153, 2157, 2161, 2165, 2169, 2173, 2177, 2181, 2185, 2189, 2193, 2197, 2201, 2205, 2209, 2213, 2217, 2221, 2225, 2229, 2233, 2237, 2241, 2245, 2249, 2253, 2257, 2261, 2265, 2269, 2273, 2277, 2281, 2285, 2289, 2293, 2297, 2301, 2305, 2309, 2313, 2317, 2321, 2325, 2329, 2333, 2337, 2341, 2345, 2349, 2353, 2357, 2361, 2365, 2369, 2373, 2377, 2381, 2385, 2389, 2393, 2397, 2401, 2405, 2409, 2413, 2417, 2421, 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7737, 7741, 7745, 7749, 7753, 7757, 7761, 7765, 7769, 7773, 7777, 77

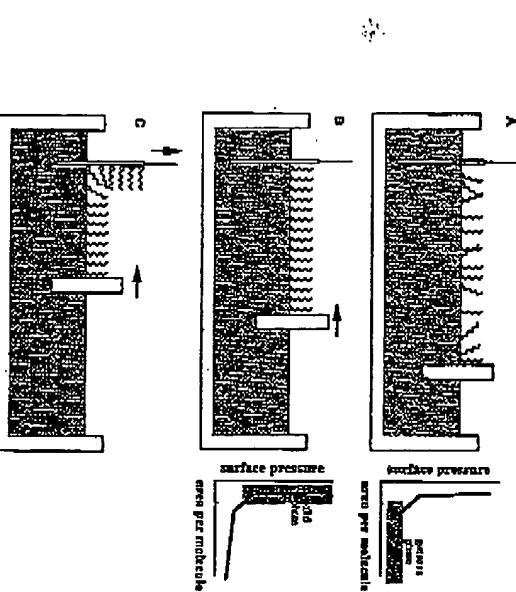


FIG. 6. Deposition of a tin film onto a polymer surface by the Langmuir-Blodgett technique. (A) The wavy film; (B) the flat film; (C) the flat film with a tin film deposited on its surface. (From Kim and Kim, 1986.)

which the SMA is being applied. The "B" block will be incompatible with the bulk material and have lower surface energy. Thus the A block will anchor the B block into the material to be modified at the interface. This is suggested schematically in Fig. 9. During animal fibrillations, the SMA ought to be distributed uniformly throughout the bulk. After a period for curing or annealing steps, the SMA will adhere to the surface. For example, an SMA for a polyethylene might have a low-molecular-weight polyethylene A block and a polydimethylsiloxane (PDMS) B block. The A block will anchor the SMA in the polymer bulk. The polydimethylsiloxane block can interact with the bulk polyethylene, while the low-surface-energy, highly flexible, siloxane B block will be exposed at the air surface to lower the interfacial energy (more that air is "hydrophilic"). The A block should confer stability to the system. However, if the system is placed in an aqueous environment, a hydrophobic-copolymer (e.g., polyurethane) is now in contact with water—a high interfacial energy situation. If the system,

obst. fibrillation, still exhibits sufficient chain mobility, it might prefer to bring the bulk polyethylene or the A block to the surface. Unless the system is specifically engineered to do such a surface phase reversal, this inversion is undesirable. Proper choice of the bulk polymer and the A block can mitigate surface phase inversions.

Many SMAs for biologic systems are known. For example, very small quantities of gold will completely alter the structure of a silicon (111) surface (Yoshida and Chikaiishi, 1987). Copper will accumulate at the surface of gold alloy (Nezu et al., 1983). Also, if tin exists as a solid aluminum-rich intermetallic compound with the bulk polyethylene, while the low-surface-energy, highly flexible, siloxane B block will be exposed at the air surface to lower the interfacial energy (more than air is "hydrophilic"). The A block should confer stability to the system. However, if the system is placed in an aqueous environment, a hydrophobic-copolymer (e.g., polyurethane) is now in contact with water—a high interfacial energy situation. If the system,

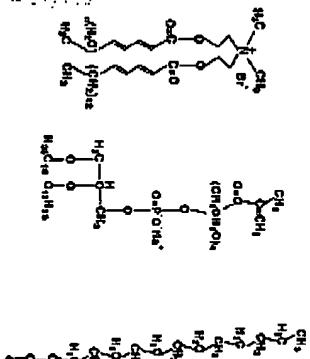


FIG. 7. Three examples of molecules that form organometallic films. (A) Polymerizable polyphenyl phosphide; (B) fatty acid; (C) transition metal complex. (With permission.)

#### Conjugated Coatings

Conjugation modifies the surface of a metal into a dense outside layer that imparts corrosion protection, enhanced adhesiveness, and increased liability to the metal. Such is frequently illustrated (coated with phenylmagnesium or dimethyl lead (e.g., stannous) in water) for up to 30 nm will provide a passivated surface (i.e., protected by its own shield).

The reason the study of these surface modifications are called organotin is that the structure is complex, including OTf, H, and antigenic sites may or may not be synergistic. Since most passive surfaces are thin films ( $50-100 \times 10^{-9}$  cm), and are transparent or metallic. In other, the surface appears similar before and after passivation. Further details on surfaces of this type can be found in Chapters 12, 22, and 23.

#### Polymer Coating

Titanium (titanosilicate) coatings occupy a unique niche in the surface modification literature because of their frequent application and the good quality of the thin film coatings. The deposit is frequently (Lob et al., 1974; Nichols et al., 1984). The deposit does not appear to be metallic. In other, the surface appears similar before and after passivation. Further details on surfaces of this type can be found in Chapters 12, 22, and 23.

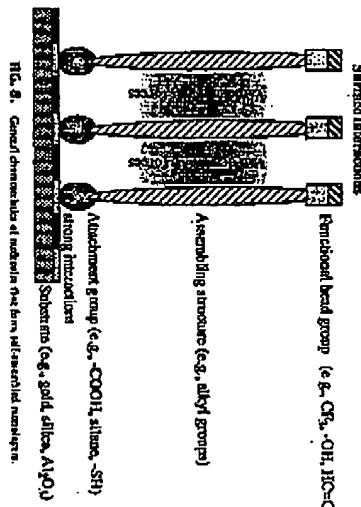


FIG. 8. General characteristics of coatings on titanium substrates. (From Kim and Kim, 1986.)

modified in chromic, oxalic, or sulfuric acid electrolytes. Anodization may also be used for surface-modifying titanium and Ti-Al alloys (Brenda, 1970; Kuroda and Iizumita, 1983).

The conversion of metal surfaces to "oxide-like" electro-

chemically passivated surfaces is common practice for bone-metal alloy implants in biomaterials. Standardized recommended techniques have been published (e.g., ASTM F-46) and are relevant for most anisotropic rough-bearing surgical implants. The background literature supporting these types of surface passivation technologies has been summarized (Kim, 1986).

Passive metal alloy systems, in general, are subject to electro-

lytic corrosion ( $M \rightarrow M^{+} + e^{-}$ ) within saline environments. The rate of this corrosion process is reduced 10–100 times by the presence of a internally conductive, relatively inert oxide surface. For many metallic devices, exposure to a nitric acid (e.g., sulfuric acid in water) for up to 30 min will

cause a passivated surface (i.e., protected by its own shield).

The reason the study of these surface modifications are

called organotin is that the structure is complex, including OTf, H, and antigenic sites may or may not be synergistic.

Since most passive surfaces are thin films ( $50-100 \times 10^{-9}$  cm), and are transparent or metallic. In other, the surface appears similar before and after passivation. Further details on

2

2 CLASSES OF MATERIALS USED IN MEDICINE

during Fabrication

FIG. 9. A block copolymer representing a rubber solution as a black liquid similar to a block rubber latex in a spirit mixture (the bridge with a density trend throughout the polymer). The black component has a density of 1.06 and the white component has a density of 0.96. After cutting or annealing, the A block undergoes a reversible phase transition between two states reported with the same density.

extraction, probability, description, and interpretation of the measure, class, characteristic, and information that the measure provides. After writing or reading a block, I always go back and make sure that each sentence has a point, that the segment makes sense, and that the segment adds to the overall message.

**reaction**: hydrolysis, depolymerization, and fragmentation of the polymer melt, cf. *parametrization (PPN)*, according to the following reaction:

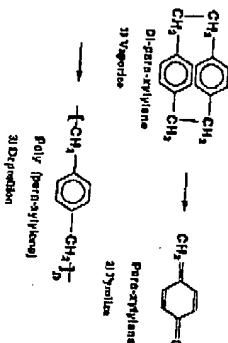
$$D(\text{block}) \rightarrow n_1 D + n_2 \text{block}$$

the incompatibility of some medical devices and in vitro diagnostic reagents have appropriate performance characteristics, physical properties, and sufficient familiarity, surface modifications can result in a means to alter only the biocompatibility of the device without the need for redesign, resulting for minuscule, and attenuating of medical personnel.

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## 2.10 FABRICS

Shalaby W. Shalaby

The use of fabrics and other fibrous forms as biomaterials dates back to the early Egyptians and Indians. Linen sutures and strips was used by the Egyptians with natural adhesives to draw the edges of wounds together to achieve proper healing and retention of original strength. The American Indians used horsehair, cotton, and thin leather strips (Shalaby, 1985) for a similar purpose. More recent use of fabrics as biomaterials was generally viewed as an extended application of the traditional woven and knitted forms of textiles. Prior to the development of the polyethylene terephthalate-based vascular grafts (Hoffman, 1977; Williams and Roaf, 1973), woven, nonwoven and knitted cellulosic fabrics represented the major types of fibrous materials used by the health care industry. Over the past few decades, with the development of sophisticated polymer and fiber processing technologies, nontraditional forms of fabrics, and fabriclike fibrous products have become available and used successfully as biomaterials in old and new applications (Boretos and Edeen, 1984). Hence, it is an objective of this chapter to survey the major traditional and nontraditional forms of fabric constructions and related products and provide brief descriptions of the constituent materials, their processing and properties. A list of physical and biological characterization and test methods is also provided.

### TYPES OF FABRICS AND THEIR CONSTRUCTION

Textile fabrics of woven, nonwoven, and knitted types have been used in one or more biomedical applications. These fabrics are made from a wide range of natural and synthetic fibers, as described in fiber and textile science publications (Joseph, 1981, 1984; Labarthe, 1975; Moncrieff, 1975). Descriptions of these fibers and their parent polymers are given in Tables 1-A to 1-C. The processing and characterization of fabrics are addressed in detail in these publications. In a review of fibrous materials for biomedical applications by Shalaby (1985), major types of materials were highlighted. The formation and characterization of unconventional constructions (some of which are not assembled by fiber processing), such as expanded porous poly(tetrafluoroethylene) (Gore-Tex, W. L. Gore and Assoc., Inc.) and hollow fibers, are discussed in a few reviews (Collier, 1970; Hoffman, 1977; Shalaby, 1985; Shalaby et al., 1984). The characterization and testing of fibrous devices and fabric surfaces have been reported in a few reviews (Cooper and Peppas, 1982; Hoffman, 1977; Hastings and Williams, 1980). Important aspects of these constructions are outlined in Table 2.

Cellulose fibers from cotton or wood pulp are the natural fibers most commonly used in the production of biomedical fabrics and related construction. Highly absorbent cellulose fibers, obtained in recent years by fermentation, may find use in certain sanitary products such as napkins. The small production of these fibers, however, may limit their application. Although cellulose acetate and viscose rayon are less commonly used as fibers than cellulose, interest in other regenerated natu-

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